

COMBINATORIAL SYNTHESIS OF PARTICULATE MATERIALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to methods and apparatus for the rapid synthesis of different particulate materials having a controlled range of material properties such as chemistry, stoichiometry, crystallography and morphology. The particulate materials can be analyzed to select those that have the most desirable properties for a selected application. The present invention is also directed to material testing arrays (combinatorial libraries) formed by such methods.

2. Description of Related Art

10 A great deal of time and effort is typically required to discover and optimize new chemical compounds for a selected product application. The primary hindrance to rapid development of optimized chemical compounds is that it is difficult to predict the physical and chemical properties of various compounds, particularly for compounds that have been produced using different processing conditions. For example, given the number of available chemical elements and possible combinations of elements, it is extremely difficult and time consuming to prepare and analyze the many different chemical compounds that can be formed.

15 A technique referred to as combinatorial synthesis has been developed in recent years as a means to synthesize many different chemical compounds in a relatively short time. The different compounds can then be analyzed for one or more material properties.

20 For example, U.S. Patent No. 5,776,359 by Schultz et al. discloses a method and apparatus for the preparation of a substrate having an array of diverse compounds in predefined regions on the substrate. To form the array, a predetermined amount of a first component of a material is selectively deposited onto portions of a substrate and a predetermined amount of a second component is separately deposited onto the same substrate portions, wherein the amounts of the first and second component are different at different portions of the substrate. The components can be deposited by a thin-film technique such as CVD or sputtering, or by a solution-depositing device such as a micropipet or inkjet. The resulting substrate is reacted and can then be analyzed to determine which material has the most advantageous properties for a selected application.

U.S. Patent No. 6,013,199 by McFarland et al. is directed to the fabrication of a plurality of phosphor materials using a combinatorial synthesis method similar to that disclosed in commonly assigned U.S. Patent No. 5,776,359. A combinatorial array of chemically distinct compounds is synthesized on a silicon substrate using either an electron beam evaporation system or a sol-gel technique. In the electron beam technique, combinations of masks and shutters are used to control deposition of materials on to predefined regions of the substrate. In the sol-gel technique, sol-gel precursor solutions are deposited onto a substrate to form the array. The arrays are annealed to induce formation of the desired phases.

U.S. Patent No. 6,045,671 by Wu et al. also discloses a combinatorial synthesis technique that utilizes thin-film deposition to form the array. A physical masking system is utilized to create arrays of resulting materials that differ slightly in composition, stoichiometry and/or thickness. It is disclosed that the process can be utilized to form covalent network solids, ionic solids and molecular solids.

The foregoing methods are limited to the formation of either a thin film of the material or a small well containing a bulk material. The analysis of thin films and bulk materials do not always provide a good indication of the properties of the material in particulate form, which is the form often used in a final product. For example, the morphology of the particulates can strongly influence the properties of the final product. Further, to form materials having different ratios of their components, it is often necessary to use multiple deposition steps. It is also difficult using the foregoing methodologies to thoroughly examine the affect of synthesis temperature or other process variables on the properties of the material.

There exists a need for a rapid and economical method for producing chemical compounds of varying chemistry and/or stoichiometry in particulate form, i.e., in the form of a powder. It would be advantageous to have a method that is adaptable to fabricate many different particulate compounds with different chemical formulations. It would also be advantageous if the affect of the reaction conditions, such as reactor temperature, could be analyzed.

SUMMARY OF THE INVENTION

According to one embodiment of the present invention, a method for the fabrication of a plurality of particulate materials is provided. The method includes the steps of continuously providing a precursor composition to a reactor, continuously reacting the

precursor composition in the reactor under at least one reactor condition to form reacted precursor particles and collecting the reacted precursor particles, wherein at least one of the precursor composition and the reactor condition is varied on a real-time basis such that the reacted precursor particles comprise a first reacted precursor portion at a first time and
5 a second reacted precursor portion at a second time and at least one material property of the first reacted precursor portion is different than one material property of the second reacted precursor portion.

For example, the precursor compositions or the reactor conditions can be varied on a real time basis such that the first reacted precursor portion has a different chemical
10 composition than the second reacted precursor portion.

According to another embodiment of the present invention, a method for the fabrication and analysis of particulate materials is provided. The method includes the steps of providing a precursor composition comprising at least a first precursor component and a second precursor component to a reactor, continuously reacting the precursor
15 composition under at least a first reactor condition to form reacted precursor particles wherein at least one of the precursor composition and the reactor condition is varied on a real-time basis such that the reacted precursor particles comprise a first reacted precursor portion at a first time and a second reacted precursor portion at a second time and at least
20 one material property of the first reacted precursor portion is different than the one material property of the second reacted precursor portion and analyzing the first reacted precursor portion and the second reacted precursor portion for at least one material property.

According to another embodiment of the present invention, a method for selecting a particulate material having a desired property is provided. The method includes the steps of continuously providing a precursor composition to a reactor in the form of precursor
25 droplets dispersed in a carrier gas, reacting the dispersed precursor droplets in a reactor under at least one reactor condition to form reacted precursor particles dispersed in the carrier gas and measuring at least one material property of the reacted precursor particles while the reacted precursor particles are dispersed in the carrier gas, wherein at least one of the precursor composition and the reactor condition is varied on a real-time basis such
30 that the reacted precursor particles comprise first reacted precursor particles at a first time and second reacted precursor particles at a second time and at least one material property of the first reacted precursor particles is different than at least one material property of the second reacted precursor particles.

According to another embodiment of the present invention, a method for the

continuous fabrication and measurement of a plurality of particulate electrocatalyst compositions is provided. The method includes the steps of providing a precursor to an electrocatalyst composition comprising at least a first precursor component and a second precursor component, reacting the precursor to form a particulate reacted precursor and
5 collecting the particulate reacted precursor, wherein the step of providing a precursor composition comprises controllably changing the precursor composition during the fabrication method such that the reacted precursor composition comprises at least a first electrocatalyst composition at a first time and a second electrocatalyst composition at a second time.

10 According to yet another embodiment of the present invention, a method for the continuous fabrication and measurement of a plurality of pharmaceutical particles is provided. The method includes the steps of providing a precursor to a pharmaceutical composition comprising at least a first pharmaceutically-active precursor component and a second precursor component, generating precursor droplets from the precursor and
15 reacting the precursor to form pharmaceutical particles, wherein the step of providing a precursor composition comprises controllably changing the pharmaceutical composition during the fabrication method such that the pharmaceutical composition comprises at least a first pharmaceutical composition at a first time and a second pharmaceutical composition at a second time.

20 These and other embodiments of the present invention will be apparent from the following description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a flowsheet of a method for the deposition of a plurality of
25 materials according to an embodiment of the present invention.

Fig. 2 illustrates the variation in precursor concentration during fabrication of a plurality of materials according to an embodiment of the present invention.

Figs. 3a-3c illustrate the deposition of patterns of reacted precursors according to various embodiments of the present invention.

30 Fig. 4 is a photomicrograph of an array of phosphor particles that have been deposited onto a substrate.

Fig. 5 is a photomicrograph of one of the regions of phosphor particles illustrated in Fig. 4.

Fig. 6 is a photomicrograph of a linear feature consisting of phosphor particles deposited on a substrate.

Fig. 7 illustrates a testing probe for the analysis of reacted precursors according to an embodiment of the present invention.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method for the fabrication of a plurality of different particulate materials as well as combinatorial libraries of different materials that are designed for analysis to identify the particulate material having the best properties for a selected application. One or more process variable is changed in a controlled manner on a real-time basis such that a plurality of different materials is formed. For example, the different materials can be fabricated by changing the chemical composition of the precursor during fabrication or by changing the conditions under which the precursor is reacted.

As used herein, the term *material* broadly refers to inorganic compounds, organic compounds or materials consisting essentially of a single component, such as substantially pure metals or semiconductors. The term *chemical compound* refers to an organic or inorganic material that includes two or more elements that are chemically combined. Examples include metal oxides, polymers, metal alloys and the like. The term *material composite* refers to a combination of two or more materials within a particle. The phases may be distinct chemical phases (e.g., two different chemical compounds) or may be two distinguishable crystalline phases of the same or similar material. Examples include polymorphs (two distinguishable crystalline phases of the same material) or metal-carbon composites for electrocatalyst applications that consist of a catalytically active metal and/or metal oxide dispersed on a carbon or metal oxide support.

The description of the present invention herein also refers to a reaction to form reacted precursors. Terms such as *reaction*, *react*, *reactor* and the like are used in a broad sense and can include processes wherein the starting material (i.e., the precursor) is merely heated or contacted with a gas or the like without a chemical reaction occurring. For example, the precursor may be heated or contacted with a gas to remove water or other solvents without chemically reacting the remaining components. As another example, metal powder may be supplied to a heated reactor to rapidly melt the powder or initiate an inter-diffusion reaction without chemically reacting any of the components of the metal powder. These and similar processes are included within the scope of the present

invention.

Further, the term *reacted precursor* refers to the material that exits the reactor portion of the apparatus. The reacted precursor can be a completely reacted precursor in which case substantially no further treatment is needed to fabricate the final material.

5 However, the reacted precursor can also be a partially reacted precursor wherein the reacted precursor is collected and is then further reacted or processed, such as by heating, to form the final material. Further, the precursor may be processed without the occurrence of any substantial reaction, such as when a powder precursor is simply melted in the reactor.

10 The present invention can be implemented using a number of different reactor systems. The reactor system requires a reactor capable of permitting the precursor to react on a continuous basis, such as by heating the precursor or contacting the precursor with a hot or reactive gas. The reactor system also includes means for delivering the precursor to the reactor. In one embodiment, the reactor system includes means for
15 varying the composition of the precursor on a real-time basis while the precursor is being delivered to the reactor. As used herein, *real-time basis* means that the variable, such as precursor composition, is changed without any substantial interruptions in the operation of the reactor system. In another embodiment, the conditions under which the precursor is reacted such as reaction time, reaction temperature or carrier gas composition is varied on
20 a real-time basis. It will be appreciated that the foregoing embodiments can be combined such that the reactor system provides variation of both the precursor composition and the reactor conditions on a real-time basis.

One preferred reactor system according to an embodiment of the present invention is a spray pyrolysis system. In a spray pyrolysis system, non-volatile precursors in a
25 flowable medium are atomized to form droplets and the droplets are heated to form particulate reacted precursors. The term spray pyrolysis, as used herein, can also include spray conversion wherein the precursors to a final product are only partially converted or are converted to an intermediate product. Spray pyrolysis is advantageous in that powders with complex compositions can be produced, the powders are typically unagglomerated
30 without milling, and the powders have a high purity and a homogenous composition. In accordance with the present invention the composition of the spray pyrolysis precursor, such as the ratio of different precursor components, can be varied on a real-time basis to continuously produce reacted precursor particles of varying composition.

An example of a spray pyrolysis system is illustrated in commonly owned U.S. Patent No. 6,103,393, issued on August 15, 2000, which is incorporated herein by reference in its entirety. In a spray pyrolysis system, the liquid-containing precursor is continuously atomized to form an aerosol of fine droplets that is passed through a reactor where the liquid evaporates and the precursors are converted to a reacted precursor. Spray pyrolysis can utilize non-volatile precursors such as metal salts that have been dissolved in a solvent, such as water. Although the precursor is in flowable form to facilitate atomization of the precursor, particulate precursors can also be included provided that the particulates are small enough in size to be suspended and carried by the precursor droplets. Examples of such particulate precursors include particulate carbon and particulate metal oxides.

A process block diagram generally illustrating a spray pyrolysis reactor system is illustrated in Fig. 1. In the embodiment illustrated in Fig. 1, three different precursors (A, B and C) are utilized to form a three-component material. Precursor A 102, Precursor B 104 and Precursor C 106 are supplied to an aerosol generator 108 wherein the ratio of the precursors is varied on a real-time basis during the process. The precursor composition can be varied substantially continuously or can be varied in a step-wise manner (i.e., digitally). A carrier gas 110 is supplied to the aerosol generator 108 to move the generated precursor droplets 112 to a reactor 114 where the precursor droplets 112 are heated to form reacted precursors 116. The reacted precursor 116 is then carried by the carrier gas 110 to a delivery system 118 that delivers the reacted precursor 116 to a substrate 120 in a controlled manner.

The aerosol generator 108 used in such a spray pyrolysis system can be selected from a number of devices including single-fluid nozzles, two-fluid nozzles, ultrasonic nozzles and rotary atomizers. The preferred aerosol generator can be selected taking into consideration, for example, the desired particle size of the reacted precursor particles, the desired production rate and the precursor composition. Particularly preferred for many applications are ultrasonic transducers, also referred to as ultrasonic fountains. Precursor compositions having high levels of particulate precursors or a high viscosity may require a nozzle-based system to form the precursor droplets.

When the reaction variable is the precursor composition, fresh precursor of varying composition is continuously supplied to the aerosol generator 108. Thus, in the case of an ultrasonic generator, the precursor feed is continuously flowed over the ultrasonic

transducers. Precursor solution that is not generated into the aerosol can be discarded or can be recycled back to the precursor feed after adjusting the composition.

Fig. 2 illustrates the concentration of three components of a precursor composition over time as the process according to an embodiment of the present invention is carried out. The concentration of Precursor B is increased as the concentration of Precursors A and C is decreased. As a result, the reacted precursor exiting the reactor at the beginning of the process will have a composition that is high in A and C, such as a metal alloy including 34% A, 16% B and 50% C, whereas at the end of the process the composition will be high in B such as a metal alloy including 83% B and 17% C. Between the two endpoints will be a wide variety of alloys or inter-metallic compounds in the A-B-C system that can be analyzed to identify the material with the most advantageous properties for a selected application. The rate at which the concentration of a selected species in the precursor is changed can vary depending on a number of factors. Generally, the concentration of a selected species can vary from about 0.1 weight percent per minute to about 10 weight percent per minute. Although Fig. 2 illustrates a substantially continuous variation of the ratio of components in the precursor, it will be appreciated that the precursor composition can also be varied in a step-wise manner (i.e., digitally) where there is a substantially instantaneous change in the concentration of one or more of the precursors.

For the fabrication of metals, metal oxides and other metal-containing compounds using a spray pyrolysis system, soluble salts of the metal are generally preferred as precursors. Whether the precursor reacts to form a metal or a metal compound such as a metal oxide depends primarily upon the other constituents of the precursor composition and the gas composition in which the reaction takes place. Oxidizing carrier gases such as air generally produce metal oxides whereas non-oxidizing carrier gases such as nitrogen generally lead to the production of metals. Also, for example, sulfur-containing precursor compositions such as those including thioacetic acid can be used to form metal sulfides.

The precursor composition for spray pyrolysis can include metal salts such as metal nitrates, chlorides, sulfates, hydroxides, halides, sulfates, phosphates, carbonates, carboxylates or β -diketonates. For many applications, metal nitrates are preferred for their high solubility and ease of use. The precursor solution may be acidified to increase the solubility of the metal salt in the solution.

By way of example, one embodiment of the present invention is directed to the fabrication of electrocatalyst materials for analysis. Such electrocatalysts can be

composite electrocatalysts that include a catalytically active metal or metal oxide dispersed on a support.

One preferred catalytically active metal for electrocatalyst applications is platinum (Pt). Preferred precursors for platinum metal are $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (chloroplatinic acid),
5 $\text{H}_2\text{Pt}(\text{OH})_6$ (hydroxoplatinic acid), platinum amine nitrates or diamine nitrates such as $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (tetramine platinum nitrate), $\text{Na}_2\text{Pt}(\text{OH})_6$ (sodium hexahydroxyplatinum), $\text{K}_2\text{Pt}(\text{OH})_6$ (potassium hexahydroxyplatinum), platinum nitrates, PtCl_4 (platinum tetrachloride), Na_2PtCl_4 , and the like. Chloroplatinic acid is soluble in water and the solutions advantageously maintain a low viscosity. Hydroxoplatinic acid is advantageous
10 since it converts to platinum metal at relatively low reaction temperatures.

Another useful metal is palladium (Pd) and palladium precursors can include inorganic palladium salts such as $\text{Pd}(\text{NO}_3)_2$ (palladium nitrate), PdCl_2 (palladium (II) chloride), H_2PdCl_4 or Na_2PdCl_4 , complex palladium salts such as $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ or $\text{Pd}(\text{NH}_3)_2(\text{OH})_2$, palladium carboxylates and the like.

Another useful metal is ruthenium (Ru) and ruthenium precursors include Ru β -diketonates, $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (ruthenium nitrosyl nitrate), K_3RuO_4 (potassium perruthenate), Na_3RuO_4 (sodium perruthenate), $(\text{NH}_4)_3\text{Ru}_2\text{O}_7$, $\text{NH}_4\text{Ru}_2\text{O}_7$, $\text{Ru}_3(\text{CO})_{12}$ and RuCl_3 (ruthenium chloride).

Silver precursors include Ag_2CO_3 (silver carbonate), AgNO_3 (silver nitrate),
20 AgOOCCH_3 (silver acetate), silver amine nitrate complexes, silver carboxylates and silver oxalate. Gold precursors include AuCl_3 (gold chloride) and $(\text{NH}_4)\text{AuCl}_4$ (ammonium tetrachloroaurate). Nickel precursors include $\text{Ni}(\text{OOCCH}_3)_2$ (nickel acetate), NiCl_2 (nickel chloride), $\text{Ni}(\text{CHO}_2)_2$ (nickel formate) and $\text{Ni}(\text{NO}_3)_2$ (nickel nitrate). Copper precursors include copper carboxylates, $\text{Cu}(\text{OOCCH}_3)_2$ (copper acetate), CuCl_2 (copper chloride),
25 $\text{Cu}(\text{NO}_3)_2$ (copper nitrate), and $\text{Cu}(\text{ClO}_4)_2$ (copper perchlorate). Rhodium precursors can include $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (rhodium chloride hydrate), $(\text{NH}_4)_3\text{RhCl}_6 \cdot x\text{H}_2\text{O}$ (ammonium hexachlororhodium hydrate) and $\text{Rh}(\text{NO}_3)_3$ (rhodium nitrate).

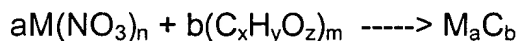
Titanium precursors include TiCl_3 (titanium (III) chloride), TiCl_4 (titanium (IV) chloride), and $\text{TiCl}_4(\text{NH}_3)_2$ (tetrachlorodiamminotitanium). Vanadium precursors include
30 VCl_3 (vanadium (III) chloride), VCl_4 (vanadium (IV) chloride), VF_4 (vanadium fluoride) and NH_4VO_3 (ammonium vanadium oxide). Manganese precursors include $\text{Mn}(\text{OOCCH}_3)_2 \cdot x\text{H}_2\text{O}$ (manganese (II) acetate hydrate), $\text{Mn}(\text{OOCCH}_3)_2 \cdot x\text{H}_2\text{O}$ (manganese (III) acetate hydrate), $\text{MnCl}_2 \cdot x\text{H}_2\text{O}$ (manganese chloride hydrate), $\text{Mn}(\text{NO}_3)_2$ (manganese nitrate) and KMnO_4 (potassium permanganate). Iron precursors include $\text{Fe}(\text{OOCCH}_3)_2$ (iron

acetate), $\text{FeCl}_2 \cdot x\text{H}_2\text{O}$ (iron chloride hydrate), $\text{FeCl}_3 \cdot x\text{H}_2\text{O}$ (iron chloride hydrate), $\text{Fe}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (iron nitrate hydrate), $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (iron (II) perchlorate hydrate) and $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ (iron (III) perchlorate hydrate).

Cobalt precursors include $\text{Co}(\text{OOCCH}_3)_2 \cdot x\text{H}_2\text{O}$ (cobalt acetate hydrate), $\text{CoCl}_2 \cdot x\text{H}_2\text{O}$ (cobalt chloride hydrate) and $\text{Co}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (cobalt nitrate hydrate). Tungsten precursors include WOCl_4 (tungsten oxychloride) and $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ (ammonium tungsten oxide). Zinc precursors include $\text{Zn}(\text{OOCCH}_3)_2 \cdot x\text{H}_2\text{O}$ (zinc acetate), ZnCl_2 (zinc chloride), $\text{Zn}(\text{OOCH})_2$ (zinc formate), and $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (zinc nitrate hydrate). Zirconium precursors include ZrCl_4 (zirconium chloride), ZrH_2 (zirconium hydride) and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (zirconium dinitrate oxide). Niobium precursors include NbCl_5 (niobium chloride) and NbH (niobium hydride). Molybdenum precursors include molybdenum chloride, $\text{Mo}(\text{CO})_6$ (molybdenum hexacarbonyl), $(\text{NH}_4)\text{Mo}_7\text{O}_{24} \cdot x\text{H}_2\text{O}$ (ammonium paramolybdate), $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ (ammonium molybdate) and $\text{Mo}[(\text{OCOCH}_3)_2]_2$ (molybdenum acetate dimer). A preferred tin precursor is $\text{SnCl}_4 \cdot x\text{H}_2\text{O}$.

The foregoing precursors can be combined in various ratios to form metal alloys having a range of alloy compositions as well as partially alloyed metal compositions. For example, platinum can be alloyed with ruthenium, tin, molybdenum, chromium or copper for electrocatalytic applications. Additives to the foregoing precursors to reduce the decomposition temperature can also be utilized. For example, ethanol or methanol added to a platinum precursor can reduce the decomposition temperature of the precursor.

The present invention is also applicable to composite particles, such as composite electrocatalyst powders. The composite electrocatalyst particles include a conductive support phase, such as carbon. In this embodiment, the precursor solution also includes at least one carbon precursor. The carbon precursor can be an organic precursor such as carboxylic acid, benzoic acid, polycarboxylic acids such as terephthalic, isophthalic, trimesic and trimellitic acids, or polynuclear carboxylic acids such as naphthoic acid, or polynuclear polycarboxylic acids. Organic precursors can react by a mechanism such as:



The use of a liquid organic carbon precursor typically results in amorphous carbon, which is not desirable for many applications. Therefore, the carbon support precursor is preferably a dispersion of suspended carbon particles. The carbon particles can be

suspended in water with additives such as surfactants to stabilize the suspension if necessary.

The carbon particulates are small enough to be dispersed and suspended in the droplets generated from the liquid precursor. Therefore, the particulates preferably have an average size of up to about 100 nanometers, such as from about 10 to about 60 nanometers when the aerosol is being generated using ultrasonics. Spray nozzles can accommodate larger particulates such as those having a size of up to about 30 μm . Particulate materials can exist in different crystallographic forms, for example carbon can be crystalline (graphitic), amorphous or a combination of different carbon types. According to one embodiment of the present invention, the type of carbon support can be varied.

After atomization of the precursor composition, liquid is removed from the droplets by evaporation in a reactor. For example, the droplets can be mixed with a hot gas to remove liquid from the droplets. A particularly preferred reactor for spray pyrolysis is a hot-wall reactor such as a tubular furnace. A hot-wall reactor transfers heat into the particle by maintaining a fixed wall temperature within the reactor zone. The carrier gas absorbs heat from the walls of the reactor until it reaches thermal equilibrium with the reactor walls. The advantages of a hot-wall reactor include the ability to control the time/temperature history of the precursor droplet/particle with greater precision over longer time intervals and the ability to achieve high processing temperatures. A hot-wall reactor is particularly useful when the reaction temperature or time is a selected process variable.

A spray pyrolysis system also enables the rapid formation of the reacted precursor. The typical reaction time in such a reactor system is less than about 10 seconds, such as from about 0.5 to about 5 seconds. Rapid formation of materials and accurate control over the time/temperature history enable precise control over the composition of the reacted precursors.

Other mechanisms such as gas-to-particle conversion (GPC) can also be used to form the reacted precursors in accordance with the present invention. Using GPC, particles are formed by nucleation and growth of low vapor pressure species. Thus, a supersaturated vapor of metal atoms is formed that condenses from the gas phase as the reactants cool. Additional precursor can decompose on the metal surface, further increasing the size of the particles. GPC utilizes either gas-phase reactants directly or utilizes volatile precursors that are dissolved in a precursor solution. In the latter case, the droplets are formed in the same way as described for spray pyrolysis, however, the solvent and the precursors completely evaporate into the gas phase before they react. GPC can

also be combined with spray pyrolysis in a hybrid process, such as where a solution containing a fuel that burns around the particles is used resulting in volatilization of the solids in the particles followed by gas to particle conversion.

The β -diketonate derivatives of most electropositive elements are volatile and after evaporation into the gas phase thermally decompose to form the corresponding metal oxide. For example, Mg, In, Sn and Ce β -diketonates are all volatile compounds that are suitable for GPC. Other examples of compounds that can be used as GPC liquid precursors include metal halides, amides, alkoxides, metal alkyls or carboxylates. The resulting particulate reacted precursors generally have an average particle size that is smaller than the particles produced by spray pyrolysis and the average particle size is typically from about 1 nanometer to about 500 nanometers.

The present invention is particularly useful for investigating various precursors and reaction conditions used in GPC formation of particles since it is very difficult to predict the composition and morphology of particles produced using such methods due to the non-linear reaction characteristics of the nucleation and growth and the diffusional mechanisms.

According to one embodiment of the present invention, supported electrocatalysts such as platinum on carbon can be formed by GPC. For example, a platinum precursor such as platinum β -diketonate or $\text{Pt}(\text{PF}_3)_4$ (platinum tetrakis trifluorophosphine) can be heated to volatilize the platinum precursor which is dispersed in a gas phase with carbon particles or the volatilized platinum precursor can be contacted with a bed of carbon particles. The platinum precursor decomposes to form platinum atoms in the gas phase which will then deposit on the carbon particles as the reactants cool, forming composite particles wherein the metal is dispersed on the support.

In addition to the foregoing, virtually any reactor system that permits real-time control over the precursor composition and/or real-time control over the precursor reaction conditions can be utilized in accordance with the present invention. For example, a thermal plasma reactor can be utilized. In a thermal plasma reactor, a high temperature plasma is used to provide the energy required for particle formation and growth. A plasma is a system with a high energy content in which a significant fraction of the species are ionized and are conductors of electricity. Precursors can be introduced to the plasma as powders or as gaseous reactants. Plasma reactors typically completely vaporize and dissociate the reactants into their atomic form. Gaseous species can nucleate to form particles as the gas is cooled upon exiting the plasma. Plasma reactors can be particularly

advantageous for the formation of materials having a high melting point, such as non-oxide ceramics. Plasma reactors can also be used to form composites such as platinum metal on carbon or platinum metal on a metal oxide.

Other reactor systems that can be used according to the present invention include those that form molten droplets of a material. Examples include plasma spray systems, flame spray systems and systems utilizing molten-metal atomization and spraying. In these reactor systems, particles of a solid precursor are melted and deposited, after which they solidify and form a film or coating. A wide variety of metal alloys and ceramics can be fabricated using such systems. As with the foregoing reactor systems, the composition of the precursor feed (e.g., a dry powder) can be varied to form a coating having a compositional gradient or the conditions of the reactor (e.g., the temperature) can be changed to modify the properties of the coating.

It will be appreciated that a reactor system can also be used wherein no substantial reaction occurs in the reactor. For example, the hot-wall reactor may be heated to a temperature that merely removes solvent from dispersed droplets without substantially reacting the precursor components. Further, the reactor system does not necessarily supply heat to the precursor composition to form reacted precursor particles. The system could, for example, merely supply sufficient hydrogen to reduce a metal carboxylate precursor at ambient temperature. The reactor could also supply sufficient light energy to a photosensitive monomer precursor to initiate polymerization and form polymer particles. For example, monomers can be dispersed in a liquid carrier (e.g., water) and subsequently polymerized. Polymerization is initiated within the droplet when the monomer reacts under light or heat to form a polymer particulate. Free radical initiators can also be placed in solution to initiate the reaction.

The reacted precursors can also be formed by nucleation and precipitation from a liquid in a micro-reactor over a controlled time period. In this embodiment, various precursors in a flowable liquid form are mixed and delivered to a reactor that is adapted to contain the precursors for a time sufficient to permit the reaction. The reacted precursors are then continuously removed from the micro-reactor. For example, the micro-reactor could include an elongate narrow reaction chamber wherein the precursors react as the liquid flows through the reaction chamber. The micro-reactor could include heating means for gently heating the liquid and/or a reaction gas could be flowed through the reactor and in contact with the liquid as the reaction occurs. The reacted precursors can be easily separated from any remaining liquid and analyzed for material properties.

Depending on the reactor system and the reactor conditions, the reacted precursor particles can have a wide range of sizes, from 1 nanometer to 100 μm or higher. For example, particles having an average size of from about 5 nanometers to about 1 μm can be formed by GPC and particles having an average size of from about 0.5 μm to about 10 μm can be formed by spray pyrolysis. Other spray systems are capable of producing particles in the size range from about 10 μm to about 50 μm . The preferred size of the reacted precursors will depend upon the application of the reacted precursors.

Where the reactor temperature is varied during synthesis of the particles, the reactor temperature is changed at a rate that is slow enough to produce useful quantities of particulates at different temperatures but rapid enough to provide meaningful data. For example, the reaction temperature can be varied at a rate of from about 0.5°C/min to about 10°C/min, such as from about 1°C/min to about 5°C/min.

It is an advantage of the present invention that the reacted precursor can be formed while in a dispersed state. That is, the reacted precursor need not be in direct contact with a support surface when it is formed. Further, no significant diffusional mechanisms are involved in the formation of the particles since the precursors are intimately mixed during formation of the reacted precursor particles.

The reacted precursor particles can be collected in a controlled manner such that the different materials can be separately identified and tested. In one embodiment, the reacted precursor is deposited on a substrate for analysis. The deposition of the reacted precursor particles onto a substrate should be implemented such that a first portion of reacted precursor particles is delivered to a first region of the substrate and a second portion is delivered to a second portion of the substrate.

The reacted precursor particles can be delivered to the substrate using a nozzle-based system. The movement of the nozzle, the substrate or both should be controlled. For example, the nozzle can be provided with a control mechanism to control the movement of the nozzle relative to the substrate. The nozzle can also deliver the particles to the substrate in a staggered manner such that the substrate consists of an array of individual regions of material. Alternatively, the nozzle can be moved continuously in relation to the substrate to form a linear feature wherein the composition or other property of the material varies along the linear feature.

In one embodiment, the particles are collected on a long continuously moving substrate that passes under a stationary nozzle. Preferably, the substrate is flexible to enable the substrate to be rolled into a compact form. Alternatively, the substrate could be

a circular substrate that rotates in relation to the nozzle. In either embodiment, the substrate is preferably a filter material that permits passage of the carrier gas through the filter while collecting particles on the surface. For example, the filter can be a TEFLON membrane filter, TEFLON fiber filter or a glass fiber filter. TEFLON is a tetrafluoroethylene polymer available from E.I. duPont deNemours, Wilmington, DE.

For example, particles can be deposited using a nozzle by inertial particle deposition or by thermophoretic particle deposition. Using inertial particle deposition, the carrier gas stream is directed at a surface and the particles are deposited by impaction. Using thermophoretic particle deposition the particles are deposited by virtue of the thermophoretic velocity of the particles in a temperature gradient wherein the particles are kinetically driven to the cooler substrate. In some cases, the particles can also be electrically charged and deposited using an electric field.

It will also be appreciated that two different reacted precursors can be delivered to the substrate using two different nozzles or a dispenser with more than one orifice for delivering multiple reacted precursors.

The substrate can be virtually any material that is amenable to the deposition of the reacted precursor on the substrate surface and subsequent treatment, if any. Examples of acceptable substrate materials include metals, polymers, ceramics and glasses. The substrate can also include depressions or wells wherein the reacted precursor particles are deposited within the depressions to prevent inadvertent spreading of the reacted precursors to an adjacent area. Further, the substrate can include adhesive regions wherein the particles are deposited onto the substrate and the particles preferentially stick to the adhesive regions.

The relative speed of the substrate to the deposition nozzle is well-controlled to ensure that a sufficient quantity of powder is collected to enable the analysis and selection of a preferred region on the substrate. For example, the relative speed of the substrate can be from about 0.1 cm/min to 2 cm/min, such as from about 0.2 cm/min to about 1 cm/min.

Different patterns for depositing the reacted precursor on a substrate in accordance with the present invention are illustrated in Figs. 3(a) - 3(c). In Fig. 3(a), the reacted precursor **304** is collected on a substrate **302** in a staggered manner such that the reacted precursor **304** is deposited in small individual regions of the substrate **302**. The substrate **302** can include, for example, a plurality of small wells or depressions in the surface of the

substrate **302** to facilitate deposition of the reacted precursor **304** into the pre-defined regions.

The present invention advantageously enables the formation of continuously varying linear features (e.g., test strips) that cannot easily be formed utilizing combinatorial methods of the prior art. In the embodiment illustrated in Fig. 3(b), the reacted precursor is deposited in the form of individual test strips **306** on the substrate **302**. Thus, the composition of the reacted precursor at portion **A** is different than the composition of the reacted precursor at portion **B**. The test strips can be deposited onto a flat substrate or can be deposited into trenches or similar depressed features that are formed in the substrate to prevent migration of material in a direction perpendicular to the test strip.

In one embodiment, the substrate can include trenches or wells to collect the particles and a substrate cap can subsequently be placed over the deposited particles to seal them in the trench or well. The particles, for example reformer catalyst particles, can then be analyzed by passing a gas composition (e.g., methanol) through the particles and measuring the off-gas composition with a chromatograph to determine the catalytic activity of the particles.

Fig. 3(c) illustrates an embodiment similar to that in Fig. 3(b), however, the test strip **308** is substantially continuous and is patterned across the substrate **302** to make effective use of the surface area available on the substrate **302**. The composition or other material property of the reacted precursor at portion **C** of the test strip **308** is different than the composition of the reacted precursor at portion **D**.

Fig. 4 is a photomicrograph of an array of phosphor particles ($\text{Zn}_2\text{SiO}_4\text{:Mn}$) deposited on a substrate. Each of the circular portions in the array has a diameter of about 90 μm . Fig. 5 is a high magnification photomicrograph of one of the circular regions from Fig. 4. Fig. 5 illustrates that each individual region is composed of a large number of small particulates. Fig. 6 is a photomicrograph of a linear feature comprising a plurality of small particles. The average width of the line illustrated in Fig. 6 is about 90 μm and the line is composed of individual phosphor particles ($\text{Zn}_2\text{SiO}_4\text{:Mn}$).

In accordance with the present invention, the test strips can advantageously include particulate reacted precursors and the test strip will accurately mimic the properties of the material in the form in which the material is actually used. However, the test strip can also be a non-particulate coating, such as when the material is deposited as a molten material from the reactor, such as a plasma reactor system or a flame-spray system.

The deposited reacted precursor can be further reacted such as by heating the substrate to react the precursor components, such as when the reacted precursor is a partially reacted precursor. Other means for further reacting the reacted precursor include exposing the reacted precursor to a forming gas or polymerizing a deposited organic compound. In addition, it may be desirable to heat the reacted precursors at a sufficient temperature and for a sufficient amount of time to sinter or fuse the particles into solidified form.

As is discussed above, the reacted precursors can be deposited onto a substrate for analysis in a combinatorial array or as a linear feature. According to an alternative embodiment of the present invention, the reacted precursors can be analyzed on a real-time basis as they exit the reactor system. Particulate reacted precursors formed by spray devices or GPC will be suspended in a carrier gas as they exit the reactor and can be continuously analyzed for particle morphology, size or magnetic characteristics.

For example, pharmaceutical compounds in particulate form are used in inhalation devices. To ensure the accurate delivery of a prescribed amount of the pharmaceutical, the aerodynamic size of the particles must be known. The aerodynamic size of a particle is a function of the actual size, the density, the particle shape and other factors such as porosity. An aerodynamic particle size analyzer (APS) can measure the aerodynamic size of the particles in real-time as they pass through the device. The particle size can also be measured on a continuous basis by light scattering. Further, a multi-stage impactor (e.g., an Anderson Impactor) can be used to collect particles of different aerodynamic size. The collected particles having the desired aerodynamic size can then be analyzed to determine the morphology or composition that produces the desired aerodynamic diameter. The aerodynamic particle diameter can also be measured using an elutriator wherein the particles are directed down a long narrow channel and aerodynamic diameter is determined by where the particles settle out of the gas stream.

Other means for analyzing the properties of reacted precursors as they exit the reactor include applying a magnetic field to the particle stream and measuring the deflection of the particles in the field can evaluate the magnetic properties of the particles. The optical properties of the particles can also be analyzed by stimulating the particles with a light source (e.g., an ultraviolet, infrared or visible light source) and observing the light energy emitted by the particles.

As is discussed above, the present invention is applicable to a variety of materials including single component materials such as non-alloyed metals and chemical compounds.

For example, the method of the present invention can be used to fabricate single component, non-alloyed metal particles. In this embodiment, the reaction parameters utilized to fabricate the single component metal powders can be varied in order to change one or more material properties of the metal. Increasing or decreasing the reaction temperature and/or reaction time can affect the crystallinity and/or morphology of the particles. These intrinsic properties significantly influence the extrinsic properties such as electrical conductance, oxidation resistance and electromigration resistance.

The present invention can be utilized to investigate various carbon forms such as carbon nanotubes, fullerene structures and the like. Such structures can be formed from carbon precursors by GPC processes, particularly those utilizing a plasma arc for heating wherein carbon is vaporized and cooled to form unique structures. Other components can be added to form composite structures including the carbon structure, such as carbon nanotubes with a metal disposed in or on the structure. Such composite structures can be useful as an electrocatalyst. The present invention advantageously enables the rapid production of carbon structures under varied conditions such that the proper conditions for fabricating a desired structure can be identified.

The present invention is also useful for the synthesis and analysis of metal alloys or intermetallics that combine two or more metals. For example, metal alloys are often synthesized to enhance one or more of the properties of the metal. The synthesis and analysis of such metals in the form of a thin film or a bulk material yields little useful information about the metal as it is used in a device, namely in the form of a particulate.

For example, it is often desirable to alloy platinum metal with additional elements such as ruthenium to alleviate this susceptibility to carbon monoxide poisoning in catalytic devices such as fuel cells. However, the optimum alloying level of ruthenium or other alloying elements in the platinum may be different for different applications. The present invention provides a means for rapidly synthesizing and analyzing metal alloys of varying composition in particulate form.

Further, the present invention is applicable to a wide range of inorganic chemical compounds. For example, metal-oxides, -sulfides, -carbides, -nitrides, -borides, -tellurides, -selenides, -phosphides, -oxycarbides, -oxynitrides and other inorganic compounds can be

synthesized by varying the ratio of components in the precursor composition or by varying the reaction time, temperature or gas composition.

The present invention is also applicable to phosphor compounds. The properties of phosphor compounds when analyzed in the form of a thin film or bulk material do not accurately reflect the performance of the phosphor compound when it is applied in the form of a powder, such as in a display device.

Typically, phosphors include a host material (e.g., a metal oxide) that is doped with an activator ion, typically in an amount of from about 0.02 to about 20 atomic percent. According to one embodiment of the present invention, the amount of the activator ion can advantageously be varied in the precursor solution to synthesize particulate compounds having various amounts of activator ion. These compounds can then be tested under different activation energies to determine which phosphor compound has the optimum level of activator ion for a selected application. Further, different combinations of activator ions can be synthesized and tested in a similar fashion.

Phosphor compounds can be categorized by the excitation mechanism under which the phosphor compound is utilized. Electroluminescent phosphors are stimulated by an electrical source, photoluminescent phosphors are stimulated by a light source, energized electrons stimulate cathodoluminescent phosphors and x-ray phosphors are stimulated by an x-ray source.

Examples of electroluminescent phosphors that can be synthesized according to the present invention include: ZnS doped with Au, Al, Cu, Ag, Cl or Mn; M^1S wherein M^1 is selected from the group consisting of Ba, Sr and Ca and wherein the particles are doped with Eu or Ce; $M^2Ga_2S_4$ wherein M^2 is selected from the group consisting of Ca and Sr and wherein the dopant is Eu or Ce; $ZnGa_2O_4$ doped with Mn or Cr; $M^3Ga_2O_4$ wherein M^3 is selected from the group consisting of Ca and Sr and the dopant is selected from the group consisting of Ce and Eu (e.g. $SrGa_xO_y:Eu$); Y_2O_3 doped with a rare earth metal; Ga_2O_3 doped with Dy or Eu; $CaGa_xO_y$, such as $Ca_3Ga_2O_6:Eu$ or Ce; $Zn_2GeO_4:Mn$; and $Zn_2(Ge,Si)O_4:Mn$.

Examples of cathodoluminescent phosphors that can be synthesized according to the present invention include: $Y_2O_3:Eu$; Y_2O_2S doped with Eu and/or Tb; ZnS doped with Au, Al, Cu, Ag or Cl; $SrGa_2S_4$ doped with Eu or Ce; $Y_5(Ga,Al)_5O_{12}$ doped with Tb or Cr; $Zn_2SiO_4:Mn$ and Y_2SiO_5 doped with Tb or Ce.

Examples of photoluminescent phosphors that can be synthesized according to the present invention include: barium magnesium aluminate (e.g., $BaMgAl_{10}O_{17}:Eu$ or Mn); zinc

silicate (e.g. $\text{Zn}_2\text{SiO}_4\text{:Mn}$); yttria (e.g., $\text{Y}_2\text{O}_3\text{:Eu}$ or Tb); yttrium gadolinium borate (e.g., $(\text{Y,Gd})\text{BO}_3\text{:Eu}$) and barium aluminate (e.g., $\text{BaAl}_x\text{O}_y\text{:Mn}$).

Examples of x-ray phosphors that can be synthesized according to the present invention include: gadolinium-containing phosphors such as yttrium gadolinium borate (e.g., $(\text{Y,Gd})\text{BO}_3\text{:Eu}$ or Tb), gadolinium oxysulfide (e.g. $\text{Gd}_2\text{O}_2\text{S:Tb}$), and yttrium gadolinium silicate (e.g., $(\text{Y,Gd})_2\text{SiO}_5\text{:Tb}$ or $(\text{Y,Gd})_2\text{SiO}_5\text{:Tb, Ce}$).

The present invention is also applicable to the synthesis and analysis of pigment particles. It is also advantageous to measure the properties of pigments in the particulate form rather than in a thin film or bulk form since a majority of applications of pigments utilize pigment particles and the size of the pigment particles significantly influences the optical properties. The pigment particles can advantageously be deposited into a carrier material to more accurately simulate the optical properties of the particles in an actual application.

Inorganic pigments include many different compounds that are known in the art of pigments. Typically, inorganic pigments are composed of substantially water insoluble particles of transition metal oxides, e.g., oxides of the elements in Groups IIIA, IVA, VA, VIA, VIIA, VIIIA, IB and IIB of the Periodic Table. Common inorganic pigments include natural and synthetic iron oxide compounds such as Fe_2O_3 (red), Fe_3O_4 (black), $(\text{Fe,Cr})_2\text{O}_3$ (brown), ZnFe_2O_4 (tan) and FeOOH (yellow). Chrome-based pigments are also common such as lead chromate salts, Cr_2O_3 (green), zinc chromate (yellow) and strontium chromate. Other complex inorganic pigments include nickel titanate, chrome titanate, manganese titanate and cobalt chromite. Cadmium pigments based on cadmium sulfide blended with other sulfides or cadmium compounds are also known. Other sulfide pigments are based on cerium sulfide modified with other rare earths. Cobalt compounds, such as cobalt aluminum oxide (CoAl_2O_4), are commonly used for blue. Rutile (TiO_2) is the most common white pigment and is commonly used in paper, plastics, printing inks, ceramics and building materials. TiO_2 with other elements such as Sb , Ni and Cr can provide different colors. Other white pigments include zinc oxide (ZnO), lead carbonate (PbCO_3), zinc sulfide (ZnS) and antimony trioxide (Sb_2O_3). Metal nitrides can also be used as pigments. Some pigments also include a dispersion of one or more metallic phases to enhance the color characteristics of the pigments. The foregoing list of inorganic pigment compounds is for the purpose of providing common examples and the present invention is not limited to the synthesis and analysis of the listed compounds.

The present invention can also be applied to the fabrication and analysis of glass compounds for a variety of applications. For example, glass microspheres are utilized for a variety of applications. By varying the precursor composition and the reaction conditions, the optimum conditions for the fabrication of hollow particles having a selected wall thickness can be determined. Other glasses, such as sealing glasses utilized in the electronics industry can be fabricated and analyzed for properties such as the softening point and adhesion. Non-reacted glass precursors can also be fabricated and analyzed, such as those used for the fabrication of optical waveguides.

The present invention is also applicable to solder materials, which are multi-component metal alloys having a low melting temperature that are used for joining other metal structures, such as by welding. Solder compositions typically include Pb and Sn along with other elements such as In and Zn. The concentrations of the components can be varied to optimize properties such as the melting temperature of the solder alloy, the oxidation resistance of the weld, the pull strength of the weld and the like.

In another embodiment of the present invention, the method of the present invention is utilized to fabricate and analyze hard, optically transparent conductors for use in forming transparent conductive electrodes (TCE's). TCE's are utilized in devices such as electroluminescent displays and lamps, solar cells and automotive glass. For example, indium-tin oxide (ITO) is a material that is commonly used as a TCE material wherein the compound includes from about 95 to 99.5 weight percent In_2O_3 and about 0.5 to 5 weight percent SnO_2 . Other compounds include $\text{Zn}_2\text{In}_2\text{O}_5$ and other similar compounds containing the In, Sn, Zn, Sb, Mg and Ce oxides. The optical transparency and electrical conductivity of these compounds is significantly influenced by the reaction conditions and the ratio of indium to tin within the compound. According to the present invention, these variables can be controllably changed during processing and the deposited material can be analyzed for these properties. For example, the method of the present invention can be utilized to explore the ternary system of In_2O_3 , SnO_2 and ZnO .

The present invention is also applicable to the fabrication and analysis of electrocatalyst materials. One type of electrocatalyst material is a supported electrocatalyst wherein an active species such as a metal or metal oxide is dispersed on a conductive support. Preferred metals for the active species include platinum, palladium, silver, ruthenium, osmium and their alloys. Metal oxide active species can include, for example, manganese oxide (MnO_x). The performance of the supported electrocatalyst particle can depend upon a number of intrinsic properties such as the concentration of

active species and the dispersion of the active species on the support. The nature of the support can also influence the properties of the electrocatalyst particles. For example, the crystallinity of a carbon support or the porosity and pore structure of the carbon support can influence the electrocatalyst properties. The fabrication and analysis of different support materials, such as metal nitrides, metal carbides and metal borides, can also be useful. The support material can be formed in-situ or can be formed from a pre-reacted material as a precursor.

In addition, some useful electrocatalyst particles are unsupported particles. Examples include perovskite phase metal oxides such as $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$. Other useful oxides include oxygen deficient Co-Ni-O and spinels of the form AB_2O_4 where A is selected from divalent metals such as Mg, Ca, Sr, Ba, Fe, Ru, Co, Ni, Cu, Pd, Pt, Eu, Sm, Sn, Zn, Cd, Hg or combinations thereof and B is selected from trivalent metals such as Co, Mn, Re, Al, Ga, In, Fe, Ru, Os, Cr, Mo, W, Y, Sc, lanthanide metals and combinations thereof. Other electrocatalysts can be derived from molecular compounds that are either dispersed on a support phase or are unsupported. Examples include metal porphyrin complexes and other metal ligand complexes.

The present invention is also applicable to the fabrication and analysis of other catalyst materials, including reformer catalysts, hydrodesulfurization catalysts and other catalysts for chemical reactions. For example, reformer catalysts are used to convert hydrocarbons to hydrogen-rich gas mixtures for use as a fuel in fuel cells. Reformer catalysts typically include platinum, palladium, ruthenium or their alloys dispersed on a metal oxide such as alumina or ceria. The alloying components and/or their ratios can be systematically varied to fabricate a catalyst having the best properties for a selected application.

Other catalyst compositions can also be synthesized, such as those used in water-gas shift reactions, auto-thermal reforming and steam reforming. Examples of these compositions are listed in Table 1.

Table 1 Catalyst Compositions

Catalyst Formulations	Catalytic Reaction	Composition	Target Reaction Temperature	Variations in Synthesis
AuNi/ γ -alumina AuNi/MgO AuNi/SiO ₂ Reference: Ni/alumina	SR/HT WGS Goal: minimize coke formation	A) 10 wt.% Ni 0.2 wt.% Au B) 15 wt.% Ni, 0.3 wt.% Au	650°C – 700°C	Time, temperature of synthesis to vary dispersion and alloy stoichiometry
Ru/ γ -alumina	SR/HT WGS	0.1-0.3 wt.% Ru	650°C – 700°C	Time, temperature

	Goal: minimize coke formation			of synthesis to vary dispersion
Ni/CeO ₂ /γ-alumina	ATR Goal: increase conversion for diesel and selectivity for H ₂	5-15 wt.% Ni	650°C - 750°C	Time, temperature of synthesis to vary dispersion
NiRu/CeO ₂ /γ-alumina (or other oxide ion conducting support)	ATR Goal: increase conversion for diesel and selectivity for H ₂	A) 10 wt.% Ni 0.3 wt.% Ru B) 15 wt.% Ni, 0.5 wt.% Ru	650°C - 750°C	Time, temperature of synthesis to vary dispersion and alloy stoichiometry
Pt/CeO ₂ /γ-alumina	LT WGSR Goal: <0.5 % CO	0.1-0.3 wt.% Pt	200°C - 300°C	Time, temperature of synthesis to vary dispersion
PtRu/CeO ₂ /γ-alumina	LT WGSR Goal: <0.5 % CO	0.1-0.3 wt.% PtRu Pt:Ru=50:50	200°C - 300°C	Time, temperature of synthesis to vary dispersion and alloy stoichiometry

WGSR = water gas shift reaction

ATR = auto-thermal reforming

SR = steam reforming

LT = low temperature

HT = high temperature

Hydrodesulfurization catalysts can also be synthesized in accordance with the present invention. For example, the starting point for development of improved hydrodesulfurization (HDS) catalysts can be based on the catalysts that are currently available. Examples of such materials are listed in Table 2.

One of the innovative approaches according to the present invention is to intimately mix the HDS catalyst with the sulfur removal material. This involves mixing in the sense of a microchannel reactor and using the sulfur removal material (ZnO) as the support phase for the active HDS catalysts. It is feasible to combine these two into a single reactor chamber and into a single multifunctional material, because the temperature at which the NiMoS species catalytically converts mercaptans to H₂S is very similar to the temperature at which ZnO reacts to form H₂S. There is a strong benefit to having these two reactions occur in very close proximity from a diffusional and thermal integration viewpoint.

Table 2 Hydrodesulfurization Catalysts

Catalyst Formulations	Catalytic Reaction	Composition	Target Reaction Temperature	Variations in Synthesis
NiMo/ γ -alumina	HDS Goal: eliminate S-containing aromatics	15.0 wt.% MoO ₃ 3.0 wt.% NiO	400°C	Time, temperature of synthesis to vary dispersion and alloy stoichiometry
NiMo high surface area self-supporting oxide	HDS Goal: eliminate S-containing aromatics	85.0 wt.% MoO ₃ 15 wt.% NiO	400°C	Time, temperature of synthesis to vary PSD, porosity, surface area
ZnO high surface area self-supporting oxide	HDS/Sulfur removal Goal: < 1 ppm S	100 % ZnO	400°C	Time, temperature of synthesis to vary PSD, porosity, surface area
NiMo/ZnO	HDS/Sulfur removal Goal: < 1 ppm S	3 wt.% MoO ₃ , 0.6 wt. NiO 96.4 wt.% ZnO	400°C	Time, temperature of synthesis to vary PSD, porosity, surface area

The present invention is also applicable to the formation and analysis of materials useful as biological taggants or "quantum dots". These are small particles (e.g., about 1 to 10 nanometers) that are injected with biological materials such as cells with an attachment compound. The particles preferentially attach to a biological feature of interest (e.g., a DNA fragment) and can then be detected to measure the concentration of such cells. The materials are phosphors (e.g., YF₃) or semiconductors (e.g., Si-In-Ge) that emit light of a known wavelength when suitably stimulated. Changes in the material composition affect the emitted wavelength and also affect the ability of the attachment mechanism to attach to the tag.

The present invention can also be used to fabricate particles that block ultraviolet light but have low catalytic activity. Such particles are useful in sunscreen compositions. For example, the dopant level (e.g., Sb, Sn or V) in an oxide (e.g., TiO₂ or ZnO) can be varied to minimize the catalytic activity of the particles.

The present invention is also applicable to the fabrication and analysis of polymers including proton conductive polymers that are useful in membrane electrode assemblies (MEA's) for fuel cells. Such polymers can be, for example, hydrophobic or hydrophilic fluorocarbon polymers. By varying the ratio of monomers, initiators and solvents as well as the reaction conditions, the polymer with the most advantageous properties can be selected. The properties of the polymer that can be analyzed include the glass transition temperature as well as the polymer structure. The fluorocarbon polymers utilized in fuel

cells and similar devices include a polymer chain having a variety of functional groups located on the backbone of the chain. The type of functional group and the spacing and location of the functional group on the chain influences the foregoing properties.

5 The present invention is also useful for the formation and analysis of pharmaceutical powders particularly those for dry powder inhalation. Powders for dry powder inhalation require a well-controlled aerodynamic diameter, which is a function particle size, particle morphology and particle density. These properties can all be affected by the type and amount of additive (e.g., lactose) that is used to carry the pharmaceutically active compound (e.g., insulin) and form the particles. The processing conditions can also lead to
10 the formation of different polymorphs of the compounds that in turn can affect the pharmaceutical activity of the particles.

The present invention is also applicable to the fabrication of composite materials, coated materials and surface treated materials. Such material systems can include composite materials such as metal carbon composite particles for electrocatalyst
15 applications as well as coated particles. A particular example, discussed hereinabove, is a dental glass composition that is surface-treated with a silanating agent.

After deposition and post-treatment, if any, the collected materials and material systems can be analyzed for a variety of material properties. For example, test strips can be probed for conductivity, optical transparency, thermal conductivity, adhesion, hardness,
20 electromigration resistance, ferromagnetic properties, ferrimagnetic properties, dielectric properties and the like. A key feature of the present invention is that the materials and material systems are composed of powders thereby providing direct information about the relationship between chemical composition, microstructure, particle size or other chemical or morphological property and the useful properties of the material.

25 Examples of analysis devices are disclosed in U.S. Patent No. 5,776,359 by Schultz et al., which is incorporated herein by reference in its entirety. The analysis device will depend upon the property being measured and the nature of the material. Both intrinsic properties and extrinsic properties can be measured. Examples of intrinsic properties are particle size, morphology, composition, crystallinity and the like. Examples of extrinsic
30 properties include electrical conductivity, electrocatalytic activity, adhesion strength and the like. Analysis devices can include Raman spectroscopy, NMR spectroscopy, microscopy devices, RF susceptibility probes, SQUID detection devices, photodetectors and the like.

One test probe and method for analyzing the properties of an optically transparent conductor is illustrated in Fig. 7. A linear feature **702** comprising an optically transparent

conductor of variable composition is deposited onto a substrate **704** in accordance with the present invention. A probe **706** is then used to measure resistivity, after determining the cross-sectional area of the strip **702** by profilometry. Passing a laser beam **708** through the linear feature and measuring attenuation of the beam as a function of position on the feature provides a useful measure optical transmission. In this instance, the substrate **704** is glass or some other light transmitting substrate. The probe **706** and laser beam **708** are moved in a continuous fashion down the length of the test strip **702**. The data is collected and analyzed to determine which portion of the test strip **702** has the most advantageous combination of optical and electrical properties for a selected application.

While various embodiments of the present invention have been described in detail, modifications and adaptations of those embodiments will occur to those skilled in the art. Such modifications and adaptations are within the scope of the present invention.